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NATURAL GAS TO LIQUID FUELS VIA ACETYLENE

V.M. Allenger
HYDROCARBON PROCESSING RESEARCH LABORATORY

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by

V.M. Allenger*

ABSTRACT

Two alterna s are discussed for converting natural gas to liquid fuels with acetylene as the intermediate. One option, the hydrogenation of acetylene to ethylene and subsequent oligomerization of ethylene to liquid fuels can be implemented immediately. The hydropolymerization of acetylene, on the other hand, requires more research and development work before it can be considered a proven technology.

* Research Scientist, Hydrocarbon Processing Research Laboratories, Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa, K1A 0G1

LA CONVERSION DU GAZ NATUREL EN CARBURANTS LIQUIDES

par

V.M. Allenger*

RÉSUMÉ

Deux options ont été examinés pour convertir le qaz naturel en carburants liquides. La première étape des deux options est la pyrolyse du qaz naturel en acétylène. Les options diffèrent à la deuxième étape qui est la conversion de l'acétylène en carburants liquides. La première comporte l'hydroqénation de l'acétylène en éthylène suivi par l'oliqomérisation de l'éthylène en liquides et la seconde, l'hydropolymérisation de l'acétylène en liquides. La première option est une technologie viable à court terme, tandis que la deuxième ne l'est pas.

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* Chercheur scientifique, Laboratoire de recherche sur le traitement des hydrocarbures, Laboratoires de recherche sur l'énergie, CANMET, Energie, Mines et Resources Canada, Ottawa, K1A 0G1

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INTRODUCTION

Several routes exist for the synthesis of liquid fuels, e.g. gasoline, diesel from natural gas. The two commercial routes are the Fischer-Tropsch and the Mobil methanol-to-gasoline (MTG) technologies. Brief summaries of these technologies can be found in the division report ERL/ERP 84-01(TR). Both routes depend on the production of synthesis gas, a mixture of CO and H_2, by steam-reforming of natural gas. It has been shown that the reforming step accounts for as much as two thirds of the "work lost" in a methanol or ammonia plant[1]. In conventional Fischer-Tropsch synthesis using Co and/or Fe as the principal component of a composite catalyst, the carbon number distribution of hydrocarbons formed from the synthesis gas is determined by the rule of polymerization probability. Therefore, the distribution is spread over a wide range and the yield of the gasoline fraction C_5-C_{11} and its research octane number are low[2]. The Mobil technology has established a route from natural gas to gasoline via methanol. In the Mobil MTG process operating conditions are biased towards maximum conversion of methanol at the expense of product selectivity since any unreacted methanol is difficult and expensive to separate from the product stream[3]. High octane aromatic compounds account for at most 30% of the total products instead of the desired 35% yield. It is both theoretically and technically feasible, however, to manufacture liquid fuels from natural gas via a third route, i.e., by converting the natural gas to acetylene and then polymerizing and hydrogenating the products to the required fuels. Such an integrated process has never been carried out commercially although patents pertaining to this are available[4]. In the integrated process, the hydrogen used in the second phase can be obtained as a byproduct of methane to acetylene conversion.

NATURAL GAS PYROLYSIS TO ACETYLENE

THERMODYNAMIC CONSIDERATIONS

Production of acetylene by pyrolysis of methane has three requirements. Large quantities of energy must be supplied at relatively high temperatures in the shortest possible time followed by immediate cooling to temperatures below 700 K. Acetylene at 1500 K is more stable than CH_4 or the alkenes. However, if the reaction time exceeds 10 ms, then the acetylene decomposes to carbon and hydrogen, the true thermodynamic equilibrium products. In practice, the further dissociation of acetylene is retarded by keeping its partial pressure low with the use of diluents.

The following series of reactions have been postulated[5]:

$$2CH_4 \xrightarrow{k_1} C_2H_6 + H_2 \qquad (1)$$

$$C_2H_6 \xrightarrow{k_2} C_2H_4 + H_2 \qquad (2)$$

$$C_2H_4 \xrightarrow{k_3} C_2H_2 + H_2 \qquad (3)$$

$$C_2H_2 \xrightarrow{k_4} 2C + H_2 \qquad (4)$$

The temperature dependence of reaction rate constants k_1 to k_4 is shown in Figure 1. At high temperatures, reaction 1 proceeds much more quickly than reaction 4. The lower activation energy for the last reaction (30 kcal/mol) compared with the first (91 kcal/mol) makes it possible theoretically at high temperatures, to obtain high yields of acetylene from methane. The maximum conversion of methane to acetylene as a function of temperature and time is shown in Figure 2. Several methods have been used on a bench scale, a pilot scale and in industry to achieve these severe restrictions, including electric arcs[6], plasmas[7] and resistance heaters[8]. All of these methods are necessarily energy intensive. Commercial petrochemical acetylene processes in use today are described below.

COMMERCIAL PROCESSES

Acetylene has been made commercially by pyrolysis of natural gas, via several routes, namely regenerative pyrolysis[5], electric arc[6], plasma arc[7], partial oxidation[9] and cracking[5]. The existing processes are summarized in Table 1. In the regenerative method, the furnace functions by heat exchange of the cracked gases with the refractory material of the furnace. Hydrocarbons are generally cracked at 1150°C and 50 kPa using steam as diluent. After acetylene has been separated from the product gases, part of the residual gas is burned to reheat the refractory alumina furnace. Deposition of tars and carbon is not a problem in this process since they are burned off as fuel. The process is also very flexible since by controlling the operating conditions and feedstocks, it can be tailored to either acetylene or ethylene production. In the electric arc process, the energy is supplied very rapidly to the natural gas by electric current. Because of this, significantly higher yields of acetylene are obtained in arc processes than in regenerative or partial oxidation processes. However, the arc process is known to be sensitive to process variations and can lead to large amounts of undesirable carbon formation when operating poorly. In the plasma arc method, hydrogen (or argon) preheated to about 1000°C is decomposed in an electric arc to generate hydrogen atoms. The natural gas is then injected into the plasma of H radicals (5000 K) outside the arc where, as they are further cooled, they recombine to molecular hydrogen and release the energy which cracks the hydrocarbon to acetylene. In the partial oxidation process (also known as single combustion process), incomplete combustion of preheated natural gas with oxygen supplies the energy necessary to attain 1500°C. In the cracking process or the two-stage combustion process, lower value fuel gases are burned with oxygen in an initial zone to generate hot combustion gases at about 2250°C. The natural gas feed is injected into these combustion gases in a second stage and is pyrolyzed to acetylene. The partial combustion processes are the most popular for natural gas as a feed. Combined yields of acetylene and ethylene can reach 50% and the ethylene to acetylene ratio can be varied from 0.1 to 3[10].

Presently acetylene is being produced on a modest scale in Canada via the calcium carbide route[11] (Table 2). Byproduct acetylene is also obtained from the Petromont and Union Carbide ethylene facilities at Varennes and Montreal East respectively. In Canada capacity has not grown significantly since 1971 and the three remaining end-use areas of acetylene are acetylene black, trichloroethylene manufacture and metalworking. The calcium carbide

route has been phased out in the United States because of its inability to compete effectively with petrochemical acetylene. Because of the low demand to date for acetylene in Canada and the availability of limestone, coke and electricity in the Quebec-Ontario region the calcium carbide process has not been displaced.

PYROLYSIS RESEARCH AND DEVELOPMENT

Research and development in the area of acetylene production from natural gas is ongoing. Processes may be chosen which are electrically based and suffer no loss of feedstock carbon due to the introduction of oxygen. Happel and Kramer[8] demonstrated that if the mixture of methane and hydrogen was rapidly heated to 1700°C in a resistance furnace and then rapidly cooled by cold hydrogen to below 750°C then there was close to the theoretical yield of acetylene. Dupont has designed a new arc burner for the manufacture of acetylene[12]. Westinghouse has announced that a new industrial plasma-torch system is being developed which has significant potential in this area in Canada because of the availability of cheap electricity[13]. AVCO has an existing arc-coal acetylene process at the pilot stages which can be modified to accept a natural gas feed[14]. The manufacturing processes discussed so far have involved utilizing high temperatures to achieve the energy level necessary to convert CH_4 to acetylene. Other techniques have also been explored for acetylene production, e.g., corona and glow discharge processes[15]. Further developments in acetylene production technology from methane will accelerate the adoption of acetylene as a key intermediate in future fuel technology.

CONVERSION OF ACETYLENE TO LIQUID FUELS

The second phase of an integrated natural gas to liquids process is the conversion of acetylene to the desired liquid fuel. Equilibrium constants for some acetylene reactions are given as a function of temperature in Figure 3. In general, low temperatures favour high equilibrium constants for these reactions. In the absence of hydrogen, two competing reactions are evident, i.e., trimerization and decomposition. Acetylene decomposition to its elements is extremely exothermic (54.1 kcal/mol). The trimerization reactions of acetylene is similarly exothermic (48.6 kcal/mol). Selectivity is clearly an important variable in the conversion of acetylene to liquid fuels. Two options for carrying out this conversion are discussed.

HYDROGENATION OF ACETYLENE

The first option is outlined in Figure 4. The hydrogenation of acetylene to ethylene is an exothermic reversible reaction. Gas-phase hydrogenation has been the target of numerous studies because of its commercial and fundamental significance. Ethylene used for the manufacture of polyethylene must be free of acetylenic compounds. Traces of acetylene, typically 0.35 wt % (5000 ppm), must be reduced to less than 5 ppm in order to meet ethylene polymerization specifications. Acetylene has been hydrogenated to ethylene using various catalysts, e.g., Pd, Pt, Ni, and metal oxides. Acetylene hydrogenation over 0.04-0.4 wt % Pd on Al_2O_3 is the favored industrial process as the acetylene concentration can be sufficiently reduced while the undesirable hydrogenation of ethylene to ethane is minimized[16]. When acetylene is present in much larger concentrations, a nickel catalyst is usually used and a small amount of H_2S or a mercaptan is added to the feed to minimize hydrogenation of ethylene. This partial poisoning improves selectivity but lowers activity. Fundamental studies have also shown that the selectivity increases with rising temperature and falls with an increase in the ratio of hydrogen/acetylene. Iron, copper, zinc, cobalt and molybdenum have been used as promoters. Mixed Ni-Co-Cr on alumina is used commercially quite extensively for the hydrogenation of acetylene in raw, sulphur-containing olefin streams[17]. Temperatures typically range from 200-315°C and pressures from 0.3-1.0 MPa[18].

A unique feature of the hydrogenation of acetylene is that hydrocarbons containing more than two carbon atoms are frequently found in the products and that they sometimes constitute the major part of the products. This tendency of acetylene towards hydrogenative polymerization (also termed hydropolymerization) shortens the lifetime of the hydrogenation catalyst.

Ethylene was manufactured by the hydrogenation of acetylene in Germany under the special conditions of the war economy. Palladium on silica gel was used as catalyst in the German plants, e.g., at Gendorf and Huls. The catalyst life was 3 to 4 months, but regeneration could be carried out up to about 4 times using steam and air at 600°C. In the Gendorf plant, there were 24 reactors, each of which contained three catalyst trays. Acetylene and hydrogen were mixed with a very large excess of recycle gas (C_2H_2 ≈ 10%). The yield of ethylene was 80-85% of theory, and Pd usage was 1 kg/1600 t of C_2H_4. This process was studied again at least up to pilot plant in Japan in the early 50's.

ETHYLENE TO LIQUID FUELS

The ethylene produced by acetylene hydrogenation can be polymerized to higher hydrocarbons. Industrially, refinery streams containing propylene and butylene have been used as feedstocks to produce gasoline, diesel or jet fuel. The process used since the 1930's operates at temperatures between 200-230°C and pressures between 3-7 MPa. Mineral acids supported on inert substances, e.g., phosphoric acid on diatomaceous earth, are used to catalyze the polymerization of these olefins. Ethylene, however, has not been tested as a feedstock for the existing commercial units which use C_3 and C_4 olefins. Ethylene polymerized in the presence of 90% phosphoric acid at 250-330°C and at pressures of 5-6.5 MPa yields a mixture of paraffinic, olefinic, naphthenic and aromatic hydrocarbons[19]. Depending on the reaction conditions, the product distribution will vary. It has not yet been established whether liquids produced via this route may be used as fuels directly.

Olefin conversion to gasoline using zeolites (ZSM-5) is also being investigated by researchers at Mobil and elsewhere. It is noteworthy that propylene is much more easily converted over these catalysts, even at low temperatures (260°C) in comparison with ethylene[21].

Alternatively, linear α-olefins are produced commercially by the oligomerization of ethylene[20]. The synthesis of higher olefins (C_6-C_{16}) is based on Ziegler's ethylene chain growth chemistry work in the 1950's. Ethylene can be oligomerized in one step (20 MPa, 250°C) or in two steps (20 MPa, 100°C growth reaction, 1 MPa, 275°C displacement reaction) to longer chain olefins. The olefin product distribution from the two processes is somewhat different. The catalyst used in the oligomerization process is triethylaluminum, i.e., Al $(C_2H_5)_3$. Shell has developed an ethylene oligomerization process termed SHOP (Shell Higher Olefin Process) which is presently being used in Geismar, Louisiana and in Stanlaw, U.K. The olefins produced in this process (with the new catalyst developed by Shell) are presently destined for the chemical market, e.g., primary alcohols[22]. Higher olefins produced from SHOP would require some hydrotreatment to yield suitable jet fuel/diesel cut and possibly isomerization to improve octane number for gasoline[22].

ACETYLENE HYDROPOLYMERIZATION

The second option is to react acetylene directly to the desired liquid fuel. The reactions of acetylene and its derivatives have been studied since the initial work of Berthelot in 1858. It has long been recognized, therefore, that significant yields of liquid products could be obtained by heating acetylene to below 800°C. The effect of temperature on the volatile products obtained is shown in Figure 5 for 22% C_2H_2 in He at a pressure of 101.1 kPa. The primary reaction in this temperature range is polymerization of acetylene to complex mixtures made up largely of aromatic hydrocarbons. The production of aromatics is of particular importance because lighter aromatics which boil in the normal gasoline range have very high octane numbers and are therefore excellent gasoline blend stocks. Major quantities of benzene are found in these liquid products. Meyer identified many more components of the liquid product, e.g., toluene, xylene, styrene, indene, chrysene, and fluoranthene[23]. In general, however, the thermal polymerization of acetylene has not been used for chemical synthesis mostly because many different products, including high molecular weight products are obtained at the same time. These disadvantages are largely avoided when the reaction is carried out in the presence of catalysts. A selection of results on the conversion of acetylene to liquids over solid catalysts in tubular reactors is presented in Table 3. High liquid yields and a large benzene fraction are evident in all cases. The catalysts not only reduce the temperature at which acetylene undergoes reaction but also alter the product distribution.

Cyclization and polymerization of acetylene have been studied for specialty chemicals manufacture in the presence of a broad range of catalysts. These include transition metals, nickel carbonyls, carbonyls of other metals, organometallic catalysts, catalysts based on CrO_3 on aluminosilicate and Ziegler-Natta catalysts among others. It has been claimed that benzene has been synthesized in a full-scale plant by the trimerization of acetylene with over 90% yield of a very high purity product[24]. The conversion takes place at 100°C and atmospheric pressure over a chromium catalyst. Cyclooctatetraene is synthesized in quantitative yield following Reppe's procedure shown below[25]:

$$4\ C_2H_2 \xrightarrow[80\text{-}120^\circ C,\ 15\ atm]{Ni(CN)_2,\ THF} \text{ } + \text{ } + \text{higher ringed structures}$$

The very mild conditions for these conversions make this option encouraging.

In the presence of hydrogen, hydrocarbon polymers are formed at temperatures substantially less than that at which acetylene polymerizes by itself, even in the presence of a catalyst. Usually the same catalyst brings about both hydrogenation and hydropolymerization and reaction conditions determine which reaction predominates. An increase in temperature favours hydropolymerization because the activation energy is believed to be higher than for hydrogenation[5]. The nature and distribution of the polymers in the products of acetylene hydrogenation have been investigated using Ni/ZnO_2, nickel-pumice and nickel-alumina as catalyst[26]. The approximate distribution in terms of the carbon atoms in the polymer molecules formed over nickel-pumice in a flow system between 200-250°C is given in Table 4. The C_4-C_8 fraction constitutes approximately 60% of the products and would make a good gasoline fraction. The C_4 fraction of the polymers formed in the hydrogenation of acetylene over some alumina-supported Group VIII metals has been analyzed and is shown in Table 5. The distribution is altered substantially depending on the metal component. The temperatures for these reactions are low, 15°C-130°C. Recently, highly structured zeolites, e.g., ZSM-5, were investigated and found to convert acetylene in the absence of hydrogen to a limited number of aromatic products in the C_6-C_{13} range. However, catalyst deactivation was rapid[27]. With the addition of hydrogen to the feed stream, a significant portion of the product was non-aromatic (mainly ethylene). Polymerization of acetylene over chromium-Y zeolites in a static system in the temperature range 150-350°C and 4 kPa pressure was found to yield benzene and alkylbenzenes as the major product[28]. The catalyst was, however, badly deactivated. Catalytic investigations in the area of hydropolymerization are few. It can be seen from the few studies mentioned here that there is indeed scope for exploring the acetylene polymerization/hydropolymerization option further. More experimental work is needed in order to assess this route for the integrated process.

Catalyst development for these acetylene reactions should be initiated. Dual functional catalysts, i.e., hydrogenation and polymerization catalysts should be explored further. Zeolites, because of their shape selectivity are promising catalysts for acetylene conversion. These zeolites open up various options, e.g., cation-exchange and metal-loading, which can alter substantially the functionality of the catalyst (isomerization, cracking and polymerization). The effects of varying process parameters, e.g., temperature, pressure and space velocity on the nature of the products and their distribution should also be examined on these catalysts. Further consideration of this interesting route for the integrated process will undoubtedly be a profitable undertaking.

SUMMARY

Two options for converting natural gas to liquid fuels have been discussed. The first stage in both options is the pyrolysis of natural gas to acetylene. The options differ in the second stage which is the conversion of acetylene to liquid fuels. The first option consists in hydrogenating the acetylene to ethylene and subsequently oligomerizing the ethylene to α-olefins which can be isomerized to the desired fuel. Although the technology for the first option is available it has not been commercially proven as an integrated process. The second option considers the hydropolymerization of acetylene itself. This option requires more research and development before it can be considered a proven technology.

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Table 1 - Acetylene from natural gas, petroleum, and coal sources[10]

Typical Process	Principal Feedstock	Technology	Typical Companies
Electric arc	Methane, gas oils	Arc or plasma	Huels, Du Pont
Sachsse	Methane, natural gas mixtures	Partial combustion (one stage)	BASF, Dow, Monsanto
SBA	Methane, natural gas mixtures (1st stage): naphthas, heavier feedstocks (2nd stage)	Partial combustion (one and two stage)	SBA, M.W. Kellogg
Wulff	Natural gas, naphthas heavier feedstocks	Regenerative furnace pyrolysis (four cycles)	Union Carbide, Wulff
Montecatini	Natural gas, naphthas	Partial combustion under pressure	Montecatini, Diamond Alkali
Byproduct acetylene	Ethane, hydrocarbons, naphthas, oil	Steam cracking	Major oil and chemical companies (EXXON, Shell, Dow, Union Carbide)
Calcium carbide	Limestone ($CaCO_3$) and Coke	CaC_2 from C + $CaCO_3$: C_2H_2 from $CaC_2 + H_2O$	AIRCO-BOC, Union Carbide
AVCO	Coal and hydrogen	Hydrogen plasma	AVCO (pilot and demonstration plants)

Table 2 - Domestic manufacture of acetylene[11]

Company	Plant Location	Nameplate capacity (kilotonne/year)							
		1971	1976	1979	1980	1981	1982	1983f	1984f
Canadian Liquid Air	*	0.7	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Canadian Oxygen	Toronto	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Esso Chemical Canada	Sarnia**	1	1	1	1	1	1	0.5	
Les Produits Chimiques de Shawinigan	Shawinigan, Que ✟	26	26	26	26	26	26	26	26
Liquid Carbonic	Contrecoeur, Que	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Liquid Carbonic	Paris, Ont.	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
Petromont ‡	Montreal East**	1	1	1	1	1	1	1	1
Petromont ‡	Varennes, Que**	1.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
Petrosar	Sarnia	-	-	3.1	3.1	3.1	3.1	3.1	3.1
Union Carbide Canada	#	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
Total capacity		34	35	38	38	38	38	37.5	37

*plants at Regina, Winnipeg, London, Ont. and Varennes, Que: # plants at Vancouver, Vernon, B.C., Edmonton, Calgary, Saskatoon, Sask, Thompson, Man., Winnipeg, Thunder Bay, Ont., Oakville, Ont, Arvida, Que., Lauzon, Que., Sept-Iles, Que., Saint John, NB, Halifax: ‡ owned by Union Carbide Canada and Gulf Canada respectively prior to 1980: **by product acetylene from ethylene plants operated by Gulf Canada until its sale to LPCS in July 1982: ✟ Esso closed its liquids cracker in mid-1983

Table 3 - Maximum liquid yields reported from acetylene pyrolysis

Reference	Reactor	Packing	Temperature °C	Per cent by weight C_2H_2 converted to liquids	Weight Per cent benzene in liquids (or benzene homologs)	Comments
Meyer (1912)	Flow tubes in series	-	650	60	20	H_2 as co-reactant
Zelinsky (1924)	Flow tube (glass)	Activated charcoal	650	70	35	
Kovache & Tricot (1925)	Flow tube (porcelain)	Various packings Activated charcoal	650	70	35	
Ika & Ogura (1927)	Flow tube (U-tube)	Coke Activated charcoal	650	70	60	
Fujio (1928)	Flow tube (glass, porcelain)	Japanese acid clay	650	(82)	-	
Fischer et al. (1929)	Flow tube (porcelain)	Silica gel Activated charcoal	650	70	38	
Hague & Wheeler (1929)	Flow tube (quartz)	-	650	61	26	
Berl & Hofmann (1931)	Flow tube (glass)	Various packings CaO, SnO_2, Na_2SiO_3	740	-	30	H_2O as co-reactant
Schwarz & Bessel (1944)	Flow tube	V_2O_5 on pumice	650	22	66	CO as co-reactant
Massimilla et al. (1962)	Fluidized bed	Various packings silica sand, activated carbon silica gel, graphite, silicon carbide	650	85	60	
Li (1963)	Flow tube	glass wool	650	44.5	64	

Table 4 - Distribution of polymers formed in the hydrogenation of acetylene over Ni-pumice[26]

Number of carbon atoms C_n	Approximate yield [%]	Products identified in fraction
4	25	Butadiene
5	2	n-pentane, 2-methylbutane
6	25	n-hexane, 3-methylpentane, benzene
7	2	3-methylhexane
8	5	2-, 3-, 4-methylheptane
9-14	7	
15-30	17	
31-∞	17	

Table 5 - Composition of the C_4 products (%) from acetylene hydrogenation over alumina-supported group VIII metals (initial $H_2/C_2H_2 = 1$)[26]

Metal	T [°C]	Butadiene	1-butene	Cis 2-butene	Trans 2-butene	Butane
Pd	17.6	trace	59.3	13.5	23.3	3.9
Rh*	13.0	0.0	42.5	34.3	7.3	7.2
Pt	135	8.3	46.5	20.3	22.1	2.8
Ir	130	0.0	35.4	17.9	1.5	45.2

*Isobutene detected in product 8.7%

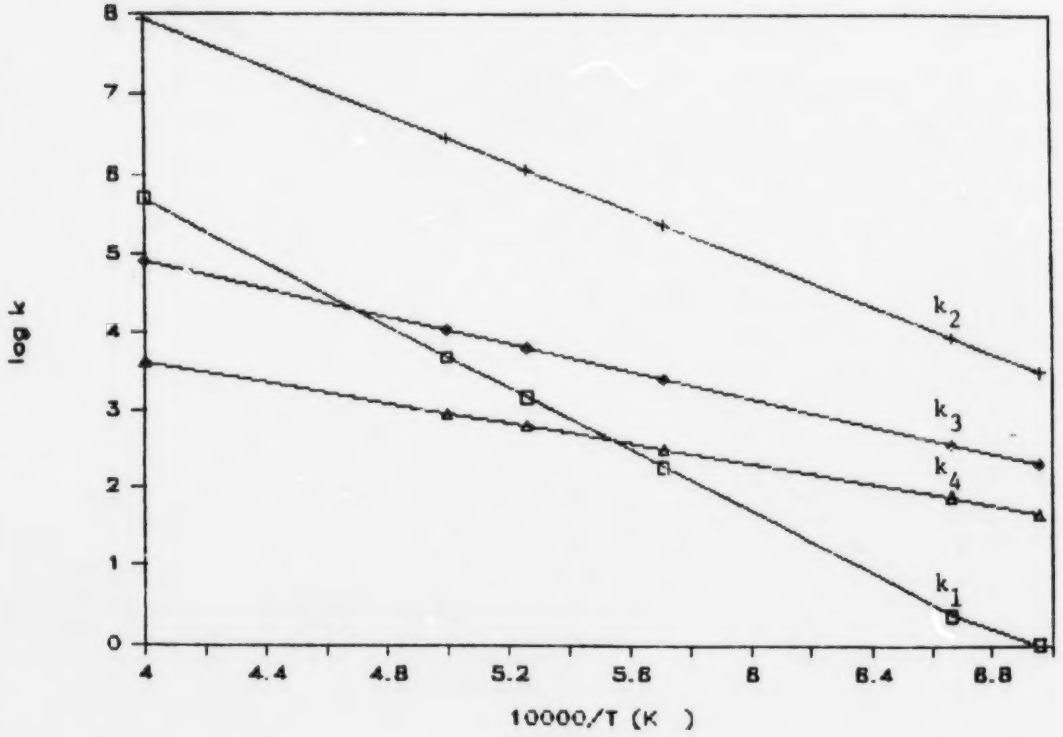

Figure 1 - Temperature dependence of reaction rate constants in the thermal decomposition of CH_4 [5]

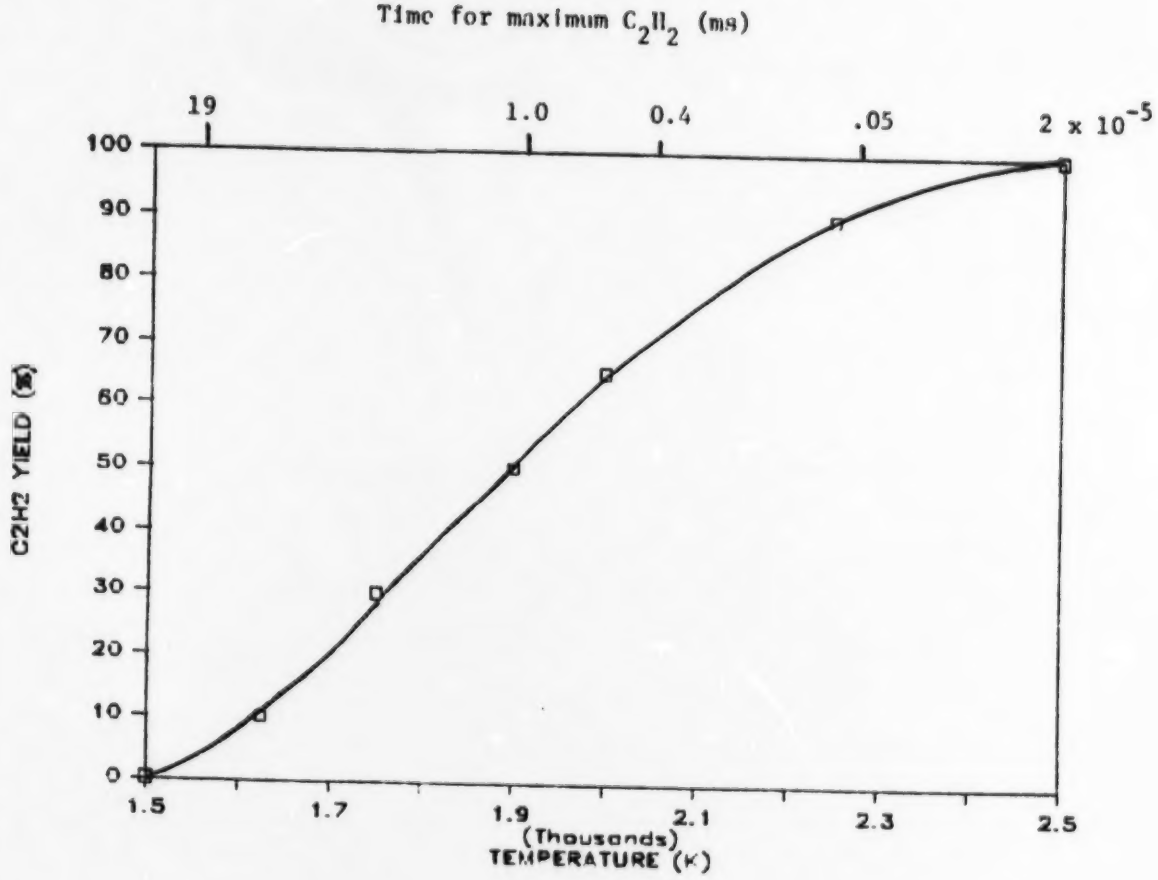

Figure 2 - Maximum conversion of methane to acetylene at various temperatures and times of the reaction[5]

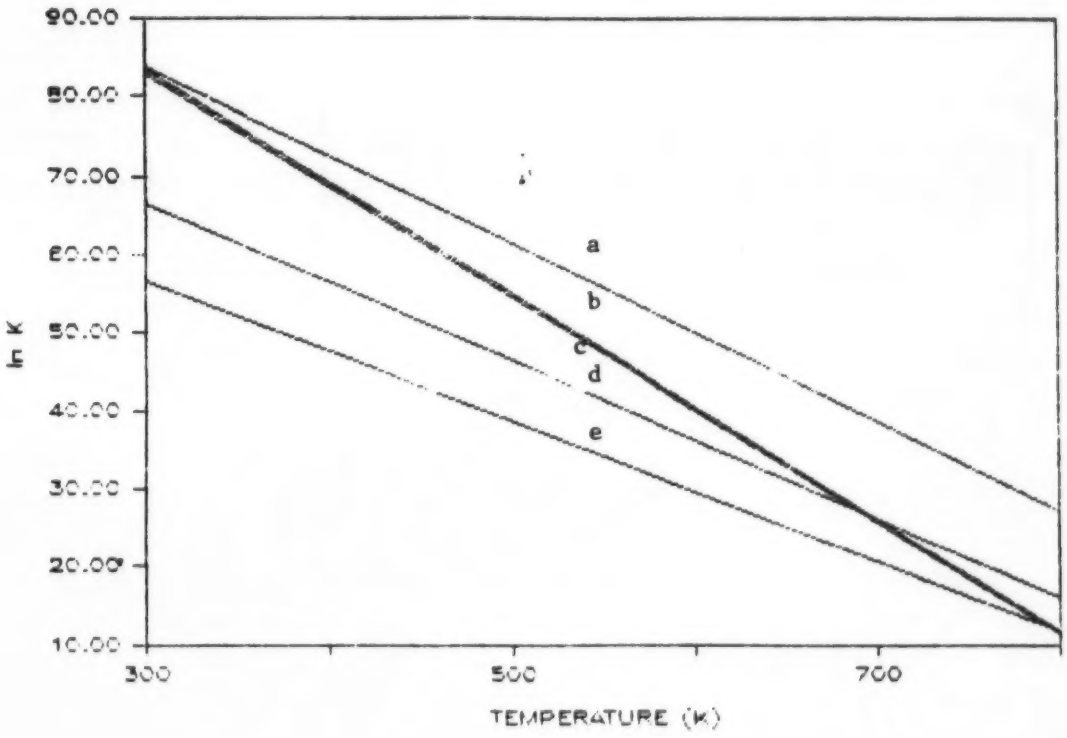

Figure 3 - Equilibrium constants as a function of temperature for the following reactions:

a	C_2H_2	→	$2C + H_2$	decomposition
b	$C_2H_2 + 4/3\ H_2$	→	$1/3\ C_6H_{14}$	polymerization
c	$C_2H_2 + 6/7\ H_2$	→	$2/7\ C_7H_{16}$	polymerization
d	C_2H_2	→	$1/3\ C_6H_6$	trimerization
e	$C_2H_2 + H_2$	→	C_2H_4	hydrogenation

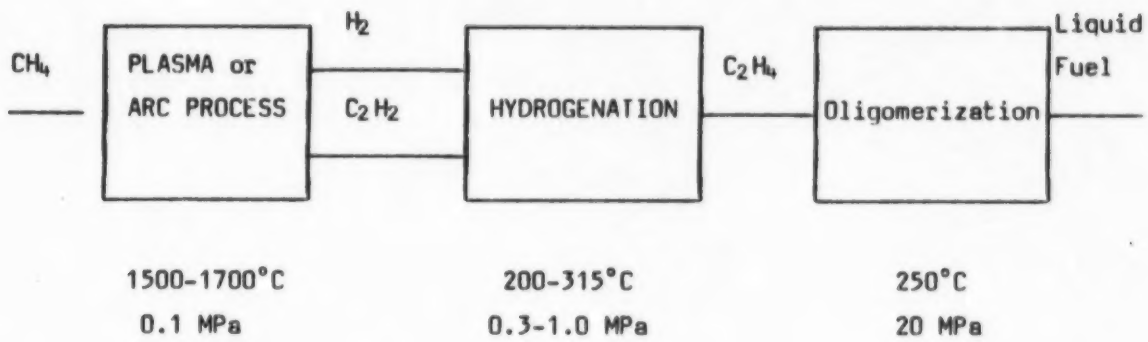

Figure 4 - Acetylene to liquid fuels: schematic of option 1

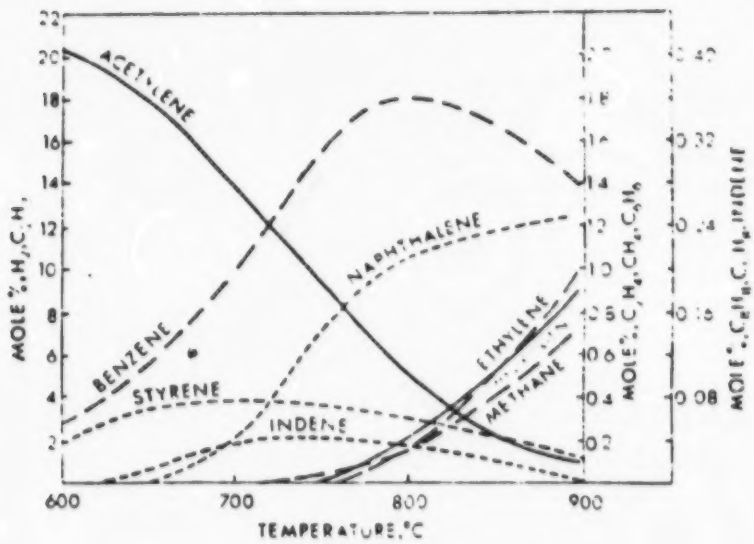

Figure 5 - Effect of temperature on the production of various hydrocarbons from C_2H_2 [5]